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Electronic structure of Y_2M_{17} intermetallic compounds

V. Crisan, V. Popescu, A. Vernes, D. Andreica, I. Burda, Simona Cristea,
Alina Olinici

Babeş-Bolyai University, Physics Department, RO-3400 Cluj-Napoca, Romania

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Abstract

Using Haydock's recursion method, the density of states was computed for Y_2M_{17} ($M \equiv Fe$, Co or Ni) intermetallic compounds, for non-ideal structures. A partial disorder was simulated displacing the Y atoms from the 2b to 2c positions and the M atoms from 4f to 4e positions. The magnetic moments, electron occupation number, electronic specific heat coefficient and Curie temperature were calculated.

Keywords: Electronic structure; Intermetallic compounds; Density of states

1. Introduction

Intermetallic compounds of R_2M_{17} type have attracted much attention because of their interesting magnetic properties [1] and their ability to dissolve large amounts of carbon and nitrogen [2–4]. To understand the influence of these interstitial atoms, it is first necessary to understand the electronic structure of the parent compounds.

As was pointed out by Gignoux et al. [5,6] and Shimizu and Inoue [7], the magnetic properties of R_2M_{17} compounds can be explained well in terms of the special shape of the total and local density of states (DOS), owing to the 3d transition metal band and 4d yttrium band hybridization and the Fermi level position.

The DOS calculations have been reported in a large number of papers using first-principles band structure calculations or the recursion method. The first self-consistent spin-polarized electronic structure calculation for rhombohedral Y_2Fe_{17} was carried out by Coehoorn [8], who found saturation magnetization in agreement with experimental data. Beuerle et al. [9] studied hexagonal Y_2Fe_{17} as well as its expanded form due to nitrogenation but without nitrogen atoms, and Jaswal [10] carried out the spin-polarized calculations for hexagonal Y_2Fe_{17} and $Y_2Fe_{17}N_3$. On the basis of the spin-fluctuation theory [11], he predicted an important enhancement of the Curie temperature upon nitrogenation. With the recursion method, DOS calculations for R_2M_{17} compounds were made by Shimizu and coworkers [7,12–14] who used for the magnetic susceptibility calculations the effect of spin fluctuations in the classical gaussian statistics [15,16]. Other calculations [17,18] took into account the intra-atomic Coulomb and spin–orbit interactions or the effect of disorder on the DOS at the Fermi level.

2. The model and method of computation

The Y_2M_{17} intermetallic compounds have the hexagonal Th_2Ni_{17} structure of space group $P6_3/mmc$. In the standard ideal structure the Y atoms are located in 2b and 2d positions and the M atoms in the 4f, 6g, 12j and 12k positions. It seems that some of the atoms, both rare earth and transition metal, are not located in ideal positions [19]. We studied the changes in the electronic structure and magnetic properties when non-ideal positions are considered. Crystallographic calculations show that the Y atoms from the 2b positions cannot occupy the 2c positions between the two occupied 4f transition metal positions. This is why at the same time a Y atom moves (from one of the 2b positions into a 2c position) and 4f atoms move (from 4f to 4e positions), resulting in two possibilities. Hence, the computations were done for three different structure types with the unit-cell parameters from experiment [20]: structure type S, the ideal Y_2M_{17} structure; structure type 1, $Y_{0.5}^{(2b)}Y_{0.5}^{(2c)}Y^{(2d)}M_{15}^{(6g+12j+12k)}M^{(4f)}M^{(4e)}$; structure type 2, $Y^{(2c)}Y^{(2d)}M_{15}^{(6g+12j+12k)}M_2^{(4e)}$. The first-nearest neighbors of Y atoms from the 2c positions are the same as from the 2b or 2d. When the 4f M

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atoms move into 4e positions, the vicinity is preserved but the interatomic distance between 4e atoms is smaller than that between 4f atoms.

The DOS was computed using the recursion method of Haydock et al. [21] and Heine [22]. The transfer integrals are expressed as functions of the two-center hopping integrals ddσ, ddπ and ddδ:

$$\mathrm{dd}m = N_\mathrm{m}\left(\frac{S}{R}\right)^5 \Delta_\mathrm{d} \qquad \mathrm{m} \equiv \sigma, \pi, \delta \tag{1}$$

where S is the Wigner–Seitz radius, R is the distance to the nearest neighbor, Δ_d is the width of the d band and N_m equals -60, 40 and -10 respectively [23]. The hopping integrals between two different atom types p and q were calculated using Shiba's [24] approximation:

$$\mathrm{dd}m_\mathrm{pq} = (\mathrm{dd}m_\mathrm{p}\ \mathrm{dd}m_\mathrm{q})^{1/2} \tag{2}$$

The potential parameters Δ and C of the linear methods of band-structure calculation were taken as the bandwidths used in (1) and as self-energies respectively. The starting point was the standard potential parameters and their volume derivatives of elemental metals [25], from which the compound parameters [26] can be computed by

$$C = C^0 + \delta(\ln S)\,\frac{\mathrm{d}C}{\mathrm{d}\,(\ln S)} \tag{3}$$

$$\Delta = \Delta^0\left(\frac{S}{S^0}\right)^{\mathrm{d}(\ln \Delta)/\mathrm{d}(\ln S)} \tag{4}$$

Thus the parametrization problem is reduced to that of finding the Wigner–Seitz radii of the atoms in compound. This was done assuming that the atomic volumes depend linearly on pressure:

$$\frac{(V_\mathrm{Y} - V_\mathrm{Y}^0)/V_\mathrm{Y}^0}{(V_\mathrm{M} - V_\mathrm{M}^0)/V_\mathrm{M}^0} = \frac{B_\mathrm{M}^0}{B_\mathrm{Y}^0} \tag{5}$$

and

$$4V_\mathrm{Y} + 34V_\mathrm{M} = V_{\mathrm{Y_2M_{17}}}{}^0 \tag{6}$$

where V_Y and V_M are the atomic volumes in compound and $V_{\mathrm{Y_2M_{17}}}{}^0$ is its unit-cell volume. Since Vegard's law is not respected [8], we used, instead of (6), $S_\mathrm{Y}/S_\mathrm{M}$ ratios of 1.25, 1.35 and 1.45 for M ≡ Fe, Co and Ni respectively. The parameters obtained were used as the first input of a self-consistent procedure with the charge-neutrality condition on each atomic site, keeping the bandwidths and Wigner–Seitz radii fixed.

The magnetic moments were calculated using the rigid-band splitting approximation [27], since they are not so sensitive to the shape of the DOS. The splitting Δ is given by

$$\Delta = \epsilon_\mathrm{F}{}^+ - \epsilon_\mathrm{F}{}^- = 2\mu_\mathrm{B}\alpha\bar{m}_\mathrm{M} \qquad \mathrm{M} \equiv \mathrm{Fe, Co\ or\ Ni} \tag{7}$$

where $\epsilon_\mathrm{F}{}^{+,-}$ are the Fermi energies for the majority and minority spin bands respectively. We assumed that

Table 1
The calculated values of average magnetic moments $\bar{m}$ and local magnetic moments for Y_2M_{17} (M ≡ Fe, Co or Ni)

Parameter (units)	Y_2Fe_{17}			Y_2Co_{17}		Y_2Ni_{17}		
	S	1	2	S	1	S	1	2
$\bar{m}$ (μ_B atom^{-1})	1.98 2.04 [13] 2.01 [32] 2.04 [33]	1.70	1.70	1.81 1.64 [30] 1.64 [13]	1.46	0.35 0.30 [31] 0.29 [13]	0.35	0.43
m, 12k (μ_B atom^{-1})	1.93 1.73 [12] 2.12 [29] 2.00 [10]	1.79	1.79	1.93 1.56 [12]	1.53	0.42 0.19 [7]	0.44	0.60
m, 6g (μ_B atom^{-1})	1.66 1.55 [12] 1.91 [29] 1.92 [10]	1.45	1.57	1.92 1.55 [12]	1.63	0.47 0.19 [7]	0.48	0.58
m, 12j (μ_B atom^{-1})	2.06 1.86 [12] 2.35 [29] 2.25 [10]	1.64	1.70	1.63 1.61 [12]	1.38	0.16 0.28 [7]	0.17	0.20
m, 4f (μ_B atom^{-1})	2.38 2.31 [12] 2.41 [29] 2.53 [10]	2.25		1.88 1.82 [12]	1.45	0.54 0.50 [7]	0.47	
m, 4e (μ_B atom^{-1})		1.66	1.60		1.13		0.45	0.35

the molecular field coefficient α is dependent on the transition metal atomic species but is independent of the structure types (S, 1 or 2). The values of α in Y_2M_{17} compounds were determined as 0.802 eV (0.966 eV [28]; 0.688 eV [12]) per Fe atom, 0.756 eV (0.77 eV [12]) per Co atom and 0.796 eV per Ni atom, yielding good agreement between the calculated and experimental values of the average magnetic moments of Fe, Co and Ni.

The spin-fluctuation theory of Mohn and Wohlfarth [11] was used for the transition temperature T_c calculation. As was pointed out by Beuerle and Fähnle [29], the theory is not able to reproduce correctly the absolute values of T_c. Consequently, only the qualitative trends of T_c when the atomic positions are changed were studied.

The low temperature specific heat coefficient was calculated from the ferromagnetic state [28].

3. Results and discussion

For all the Y_2M_{17} compounds the calculated average magnetic moments are in agreement with the experimental values (Table 1). For the Y_2Fe_{17} structures, the Fe lowest magnetic moment is for the 6g positions and the highest for the 4f positions (Fig. 1) as has already been shown in [29]. If the structure type 1 is considered, the magnetic moments are lower but their relative magnitude remains unaltered. If the structure is of type 2, the total magnetic moment per formula unit and the 4e Fe magnetic moments remain almost the same as for structure type 1.

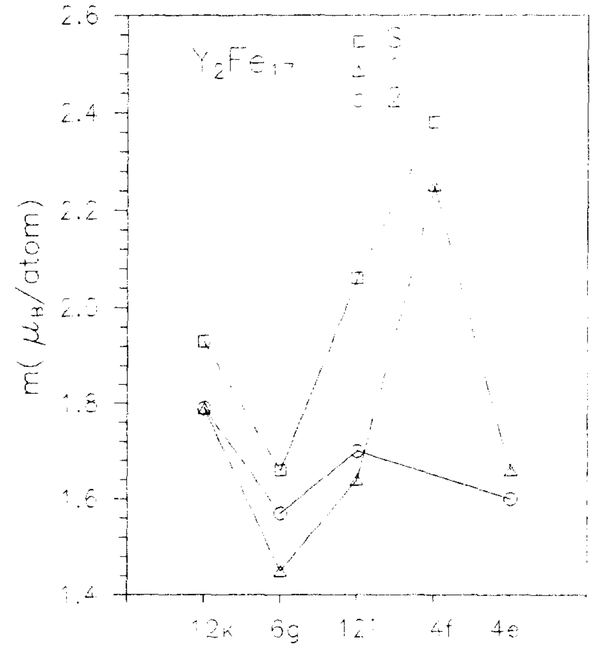

Fig. 1. Local magnetic moments for Y_2Fe_{17}.

For the Y_2Co_{17} and Y_2Ni_{17} compounds the magnetic moments show a minimum for 12j positions (Figs. 2 and 3). When the structure of the type 1 was considered for Y_2Co_{17}, the magnetic moment per formula unit decreases but remains almost constant for Y_2Ni_{17}. In structure type 2, the magnetic moment per formula unit vanishes for Y_2Co_{17} but for Y_2Ni_{17} increases. As a general feature, the 4e magnetic moments are lower than the 4f magnetic moments.

The d-orbital occupation numbers of Y atoms do not change with the structure type, while the transition

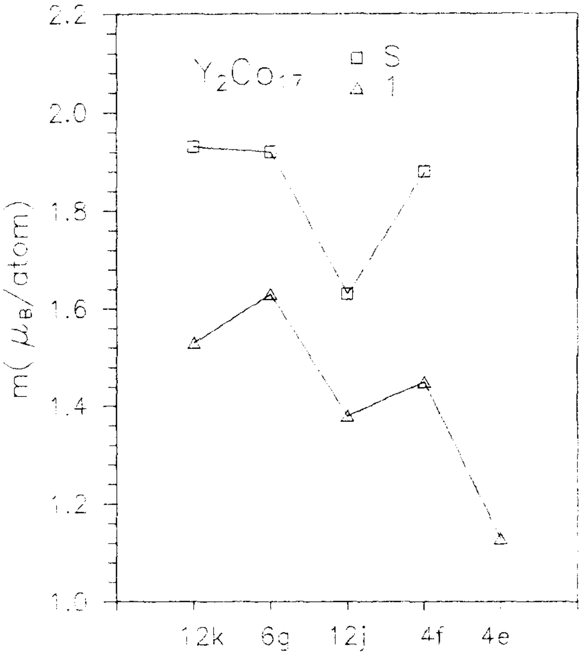

Fig. 2. Local magnetic moments for Y_2Co_{17}.

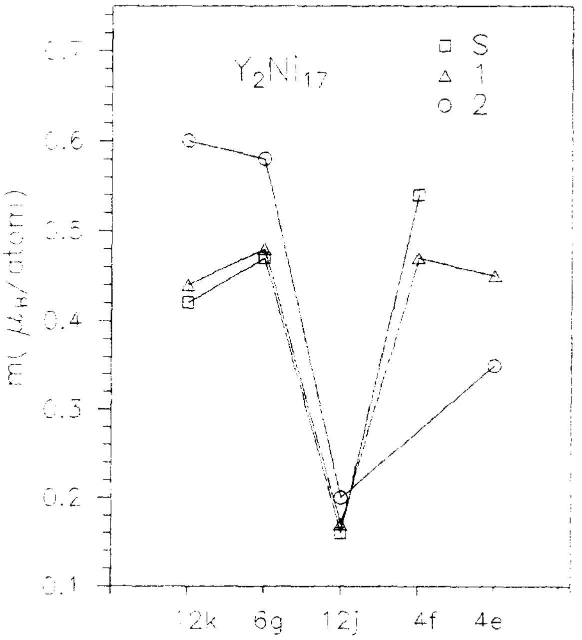

Fig. 3. Local magnetic moments for Y_2Ni_{17}.

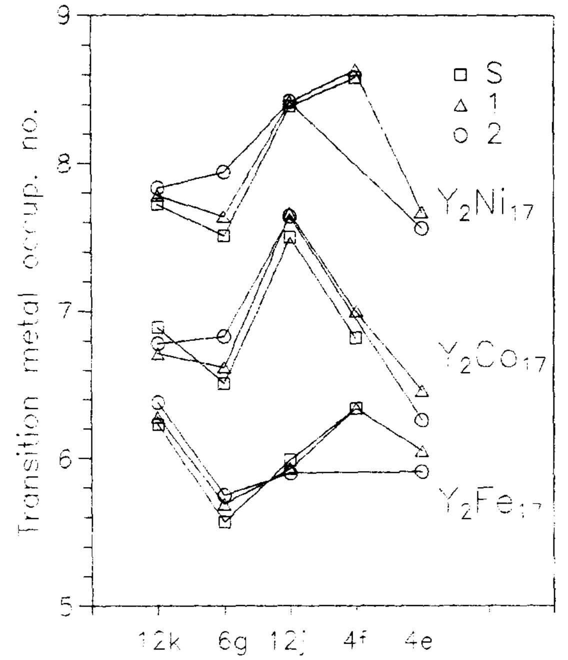

Fig. 4. The d-electron occupation numbers on transition metal sites for Y_2M_{17}.

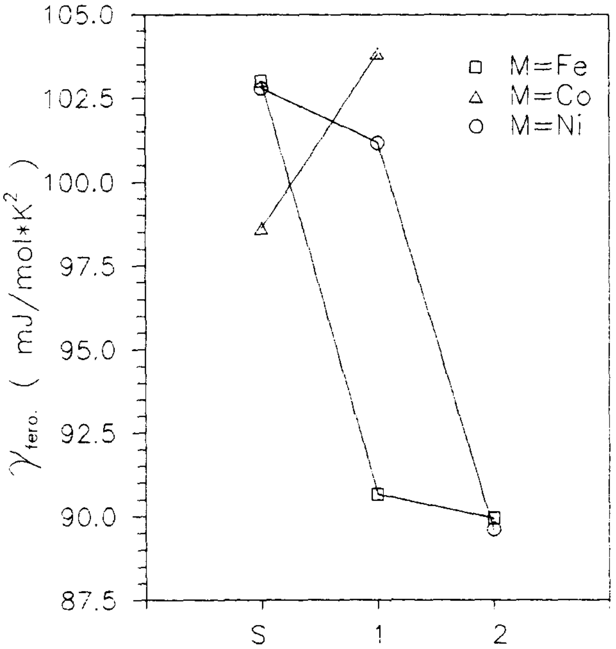

Fig. 5. The low temperature electronic specific heat coefficient for Y_2M_{17}.

metal orbital occupancy strongly depends both on it and on the crystallographic position of atoms (Fig. 4). For Ni and Fe compounds (all the structure types S, 1 and 2), the 6g atoms have fewer electrons and 4f atoms more electrons. In the Y_2Co_{17}, the maximum occupancy is for 12j positions.

The calculated Sommerfeld coefficient of specific heat for compounds in ordered phase (Fig. 5) decreases strongly for Fe and Ni, when the structure type changes from S to 1 and 2. For the Co compound the coefficient increases when the structure type changes from S to 1.

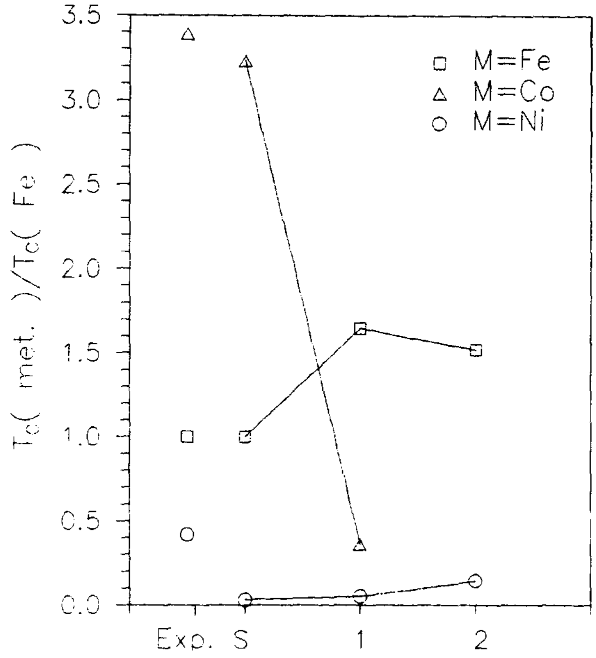

Fig. 6. The transition temperature ratios $T_c(Y_2M_{17}T)/T_c(Y_2Fe_{17}S)$, with T≡S, 1 and 2: Exp., experimental values [7].

The transition temperatures, computed for the standard structure compounds, are in agreement with the experimental values for Fe and Co compounds. In Fig. 6 are plotted the ratios $T_c(Y_2M_{17}T)/T_c(Y_2Fe_{17}S)$, for all the compounds and structure types T. For Fe compounds, the change in the structure type from S to 1 increases the transition temperature, while for Co compounds it strongly decreases. For the Ni compound, the transition temperature for the standard structure does not agree with the experimental data. This disagreement for the standard Ni compound is partly caused by the fact that the Fermi level is lying in a region with a low DOS, where the effect of the continued-fraction terminator seems to be important.

References

[1] A.V. Andreev, F.R. de Boer, T.H. Jacobs and K.H.J. Buschow, *Physica B, 175* (1991) 361.

[2] J.M.D. Coey and H. Sun, *J. Magn. Magn. Mater., 87* (1990) L251.

[3] J.P. Liu, K. Bakker, F.R. de Boer, T.H. Jacobs, D.B. de Mooij and K.H.J. Buschow, *J. Less-Common Met., 170* (1991) 109.

[4] M. Fähnle, P. Braun, T. Beuerle and K. Hummler, *J. Magn. Magn. Mater., 104–107* (1992) 1931.

[5] D. Gignoux, R. Lemaire and P. Molho, *J. Magn. Magn. Mater., 21* (1980) 119.

[6] D. Gignoux, R. Lemaire, P. Molho and F. Tasset, *J. Magn. Magn. Mater., 21* (1980) 307.

[7] M. Shimizu and J. Inoue, *J. Magn. Magn. Mater., 54–57* (1986) 963.

[8] R. Coehoorn, *Phys. Rev. B, 39* (1989) 13072.

[9] T. Beuerle, P. Braun and M. Fähnle, *J. Magn. Magn. Mater., 94* (1991) L11.

[10] S.S. Jaswal, *IEEE Trans. Magn., 28* (1992) 2322.

[11] P. Mohn and E.P. Wohlfarth, *J. Phys. F, 16* (1987) 2421.

[12] J. Inoue and M. Shimizu, *J. Phys. F, 15* (1985) 1511.

[13] M. Shimizu and J. Inoue, *J. Magn. Magn. Mater., 70* (1987) 61.

[14] M. Shimizu, M. Miyazaki and J. Inoue, *J. Phys. (Paris), 49, Colloq. C8* (1988) 297.

[15] M. Shimizu, *Phys. Lett. A, 81* (1981) 87.

[16] M. Shimizu, *J. Magn. Magn. Mater., 31–34* (1983) 299.

[17] B. Szpunar and W.E. Wallace, *Phys. Rev. B, 36* (1987) 3782.

[18] V. Crisan, A. Vernes, A. Janosi, V. Popescu and D. Kapusi, *J. Alloys Comp., 178* (1992) 379.

[19] A. Christensen and R.G. Hazell, *Acta Chem. Scand. A, 34* (1980) 455.

[20] K.H.J. Buschow, *J. Less-Common Met., 11* (1966) 204.

[21] R. Haydock, V. Heine and M.J. Kelly, *J. Phys. C, 8* (1975) 2591.

[22] V. Heine, *Solid State Phys., 35* (1980) 1.

[23] D.G. Pettifor, *J. Phys. F, 7* (1977) 613.

[24] H. Shiba, *Prog. Theor. Phys., 46* (1971) 77.

[25] O.K. Andersen, *Muffin-tin Orbital Theory, Lecture notes of the International Center for Theoretical Physics Miniworkshop, Trieste, 1992.*

[26] O.K. Andersen, O. Jepsen and M. Sob, Linear band structure methods, in M. Yussouff (ed.), *Electronic Band Structure and its Applications, Springer Lecture Notes, 1987, 72,* Springer, Berlin, 1987.

[27] H. Yamada, J. Inoue, K. Terao, S. Kanda and M. Shimizu, *J. Phys. F, 14* (1984) 1943.

[28] H. Yamada and M. Shimizu, *J. Phys. F, 16* (1986) 1039.

[29] T. Beuerle and M. Fähnle, *J. Magn. Magn. Mater., 110* (1992) L29.

[30] R. Lemaire, *Cobalt, 33* (1966) 201.

[31] X.P. Zhong, F.R. de Boer, T.H. Jacobs and K.H.J. Buschow, *J. Magn. Magn. Mater., 92* (1990) 46.

[32] R. Pfranger, D. Plusa, S. Szymura and B. Wyslocki, *Physica B, 114* (1982) 212.

[33] D. Givord, F. Givord and R. Lemaire, *J. Phys. (Paris), 32, Colloq. C1* (1971) 668.